

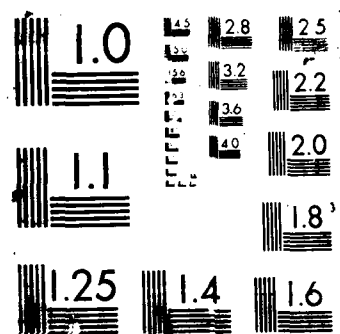
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**AD-A195 869**

## *Preliminary development of a fiber optic sensor for TNT*

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Yuke Zhang, W. Rudolph Seitz,  
Donald C. Sundberg and Clarence L. Grant

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Research aimed at the development of a fiber-optic based sensor is described for in-situ detection of TNT in groundwater. Three approaches were evaluated in depth. All three involved use of a material to concentrate TNT in the field of view of an optical fiber. The materials tested were 1) a concentrated dextran solution isolated by a semi-permeable membrane; 2) a pre-swollen cross-linked polyvinyl alcohol polymer; and 3) an amine-loaded PVC membrane. Another approach based on the formation of a colored TNT anion at high pH was also considered. The amine-loaded PVC membrane appears to have the most promise. Clear membranes were prepared which reacted with TNT to form a colored product. Measurement is made at 520 nm which is very convenient for fiber optic-based sensing. Various primary amines were assessed.					
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## Preliminary Development of a Fiber Optic Sensor for TNT

YUKE ZHANG, W. RUDOLPH SEITZ,  
DONALD C. SUNDBERG AND CLARENCE L. GRANT

### INTRODUCTION

One of the Army's most serious water pollution problems is the disposal of wash waters used to clean equipment and interior surfaces at munition manufacturing and demilitarization facilities. It has been estimated that up to two million liters of this type of wastewater is generated daily from a single production line (Walsh et al. 1973). Although this water is pumped through a carbon adsorption column prior to discharge, small amounts of compounds such as TNT remain in solution and larger amounts can escape if the lifetime of the carbon adsorption column is exceeded. Because of the possibility that these munitions can reach ground water, it is necessary for the Army to periodically determine whether ground water has been contaminated. Currently this requires that a well be drilled so that groundwater samples can be brought to the surface for analysis in the laboratory.

The goal of this project is to develop a fiber-optic-based sensing system for in-situ detection of 2,4,6-trinitrotoluene (TNT) in ground water. Successful completion of this project would reduce the need to collect groundwater samples for laboratory analysis.

The sensing system involves two components: 1) optical fibers to conduct light from a surface spectrometer to the point of measurement and back and 2) an indicator that selectively interacts with TNT to render it optically detectable through an optical fiber. In the first year of the project, we evaluated the use of concentrated dextran solutions for preconcentrating TNT in the field of view of an optical fiber for direct detection based on their absorption spectra (Shane et al. 1985). We demonstrated the feasibility of measuring UV absorption spectra for TNT through 0.6-mm-core-diam fused silica fiber. However, measurements of the degree to which concentrated dextran solutions preconcentrated TNT from aqueous solution were inconclusive and revealed serious problems. As a result, preparation of preswollen cross-linked polyvinyl alcohol was proposed as an alternative adsorbent for TNT.

In the second year of the project we succeeded in preparing a clear polyvinyl alcohol gel that transmits in the ultraviolet. However, the gel only increases the effective concentration of TNT by a factor of 1.43. Higher preconcentration factors are required if the adsorption-based sensor is to detect TNT with adequate sensitivity for ground water measurements. Because preparing gels that will give significantly higher preconcentration factors does not appear to be feasible, two other approaches to TNT sensing have been investigated.

One approach is based on the formation of a colored TNT anion in the presence of a base. In pure aqueous solution the pH must be greater than 10 to deprotonate TNT and observe color. In the presence of an anion exchanger, deprotonation is

facilitated and color is observed at pHs as low as 8. Although this approach to sensing is reversible and produces measurable color changes in the visible region of the spectrum, it is inherently pH dependent and limited to high pH. As a consequence, it was not investigated in depth.

Another approach to sensing is to use amine-doped polyvinyl chloride (PVC) membranes as indicators. TNT reacts with the amine, forming a product which absorbs strongly in the visible spectrum. The membranes are easy to make and they respond sensitively to TNT. Although the membranes do not respond reversibly, they can be used for TNT sensing on an integrating basis. When contacted by aqueous solutions, the amine tends to leach from the membranes, thereby causing cloudiness. As a consequence, current efforts are directed toward developing improved membrane formulations that will be stable in contact with water.

Separate sections of this report will describe the three approaches to TNT sensing: 1) preconcentration of TNT on a cross-linked polyvinyl alcohol gel, 2) formation of the colored TNT anion in the presence of an anion exchanger, and 3) reaction with amine-loaded PVC membranes.

## **POLYVINYL ALCOHOL GEL BASED SENSING**

### **Background**

The first sensing approach that we tried was to use concentrated dextran solutions confined by a dialysis membrane as an adsorbent to preconcentrate TNT in the field of view of an optical fiber so that absorption spectra could be measured directly. Several unanticipated problems were encountered: 1) osmotic pressure caused the dialysis membrane to swell, 2) some of the dextran leaked through the dialysis membrane, and 3) an unidentified UV-absorber leached from the membrane and interfered with absorption measurements. As a consequence, we proposed to cross-link polyvinyl alcohol (PVal) to form a preswollen gel that might adsorb TNT without being subject to the above problems. Because PVal is transparent in the ultraviolet, it does not interfere with the measurement of TNT absorption spectra.

### **Gel preparation**

The procedure for preparing the PVal gel was adapted from a method reported by Higuchi and Iijima (1985). Aqueous PVal is cross-linked with glutaraldehyde in the presence of acid as described below. To get a clear gel, it is critical that cross-linking occur slowly. Otherwise, local precipitation can cause inhomogeneities that make the resulting gel cloudy. Also, air bubbles can be trapped in the gel if cross-linking is too rapid. Both effects render the gel unsuitable for optical measurements.

The following procedure yields a clear gel. One gram of PVal (Aldrich, average molecular weight 86,000) is dissolved in 18 mL of water by gently heating and stirring for an hour. The solution is cooled to room temperature, and 160 mL of 10% glutaraldehyde (diluted from 50% glutaraldehyde from Fisher Scientific) is added and mixed. Then 0.4 mL of 1.2 M HCl is added and the resulting solution is mixed. This formulation is covered and allowed to sit at room temperature for 12 hr. The resulting clear gel is soaked in a pH 6 phosphate buffer for two days to neutralize excess acid.

Gels were usually prepared in disposable 1.00-cm plastic cuvetts. After the gel had set, the cuvet was broken apart, yielding a clear block of gel with a 1.0-cm path length. These blocks of gel were used for UV absorption measurements.



## Factors influencing gel properties

### PVal concentration

As the concentration of PVal increases, two problems develop: 1) the aqueous PVal solutions become so viscous that air bubbles escape very slowly and 2) the crosslinking reaction tends to go more rapidly. To prepare a gel from a 10% (w/w) PVal solution, the above procedure had to be modified. Aqueous glutaraldehyde/PVal and concentrated HCl were added to separate containers. Both containers were placed in a covered 500-mL beaker. The HCl was slowly transferred through the vapor phase, initiating cross-linking. Once gel started to form on the surface of the glutaraldehyde/PVal container, the concentrated HCl solution was removed from the covered 500-mL beaker and replaced with a separate container holding 0.05-M HCl. The beaker was covered again, and gel formation was allowed to proceed to completion.

### Glutaraldehyde concentration

The final water content of the gel depends on the degree of cross-linking. Swelling indices were estimated by measuring gel weight before and after soaking a 0.5-cm-thick slice of gel in water for over 24 hr. Figure 1 shows how varying the amount of glutaraldehyde affects the swelling index for the gel. These results are for gels made by combining 1.0 g of PVal in 18 mL of water and 0.4 mL of 1.2 M HCl with variable amounts of 10% glutaraldehyde. As indicated in Figure 1, the gel formed using 160 mL of 10% glutaraldehyde has a swelling index of 0. This means that the gel neither gains nor loses water when immersed in an aqueous solution. Thus this was the formulation used to measure TNT partitioning.

The ratio of PVal to water in the final gel can be increased by using higher levels of glutaraldehyde to increase the degree of cross-linking. Higher PVal levels should increase the tendency of the gel to adsorb TNT. However, it was found that increased glutaraldehyde levels caused increases in the background absorption in the ultraviolet which would limit the ability to measure TNT.

### HCl concentration

Solutions prepared by combining 1.0 g of PVal in 18 mL of water and 160 mL of 10% glutaraldehyde were reacted with 0.1, 0.4 and 0.8 mL of 1.2 M HCl. No gel was formed even after a week with 0.1 mL of HCl. Both 0.4 and 0.8 mL of HCl yielded clear gels in a reasonable period of time.

### Temperature

Gels were prepared at 12°C, room temperature and 60°C. Gel formation was accelerated at higher temperature. However, the gel that formed at the highest temper-

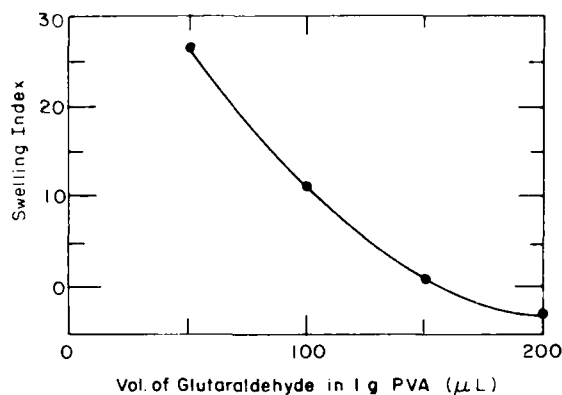


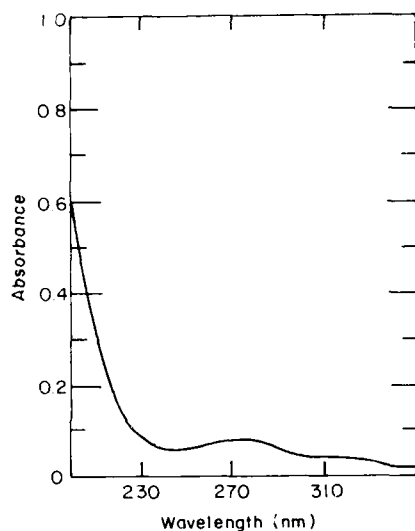
Figure 1. Swelling index for PVal gel as a function of the volume of glutaraldehyde solution added to 1.0 g of PVal. The swelling index is calculated from this formula:  $\text{swelling index} = 100 \times (\text{wt PVal after absorbing water} / \text{wt before absorbing water} - 1)$ .

ature had significantly greater background absorption of UV radiation. There was no significant difference in background between the gels prepared at room temperature and at 12°C.

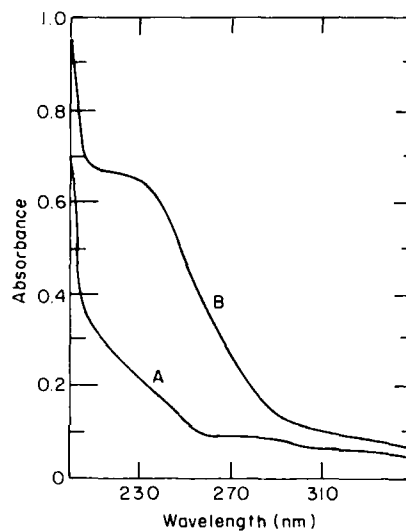
### Properties of the PVal gel

#### Absorption

Figures 2a and 2b show UV absorption spectra for PVal in solution, PVal gel and PVal gel soaked in a 0.10-mg/L TNT solution. Cross-linking leads to broadening of the major PVal absorption band in the range from 220 to 250 nm. There is also a weak band centered at 280 nm. This band, which we attribute to carbonyl absorption, actually decreases upon cross-linking. The gel is sufficiently transparent to permit measurement of TNT absorption.



a. PVal in solution prior to adding glutaraldehyde and acid.



b. PVal gel by itself (A), and after soaking in a 10-mg/L TNT solution for 10 hr (B).

Figure 2. Absorption spectra for PVal.

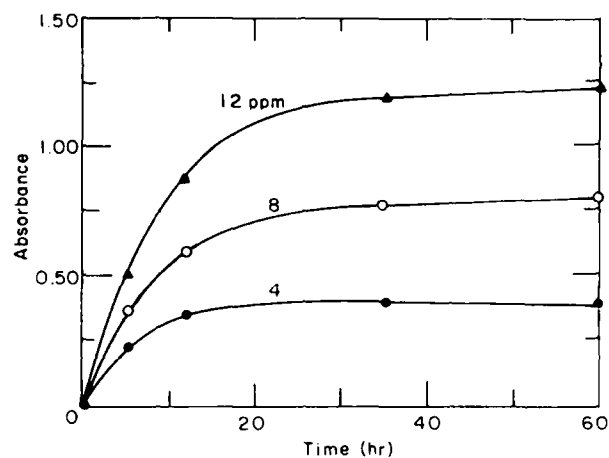
#### Stability with time

The absorption spectra of gels soaked in water or a pH 6.0 phosphate buffer do not change over a week. However, when the gel is soaked in 0.1 M NaOH, absorbance increases significantly at wavelengths shorter than 260 nm.

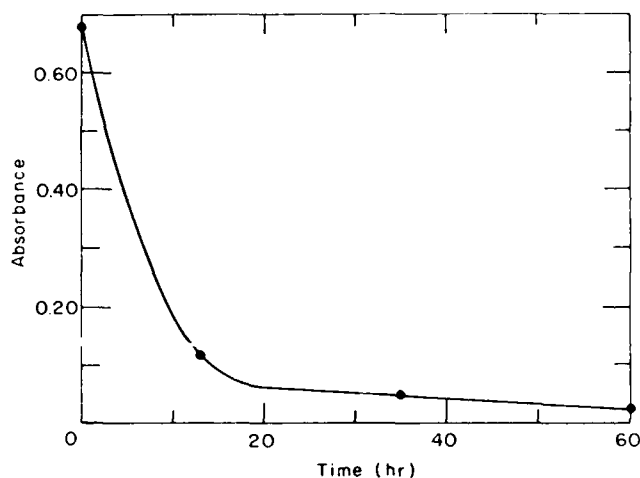
#### Response to TNT

The 1.0-cm-thick gels prepared in disposable plastic cuvetts were soaked in dilute aqueous TNT solutions. Absorption spectra measured at various times show that it takes at least 35 hr for the TNT concentration to reach equilibrium. Results appear in Figure 3a.

Figure 3b shows the decrease in TNT absorbance with time for a 1.0-cm block of gel pre-exposed to a 10 mg/L of aqueous TNT solution for 17 hr and then placed in



a. Increase in TNT absorbance for gels soaked in 4, 8 and 12 mg/L of TNT.



b. Decrease in TNT absorbance for a PVal gel in water after pre-exposure to 10 mg/L of TNT.

Figure 3. TNT absorbance with time.

water. The data confirm that the gel responds reversibly to variations in TNT concentration.

#### Partition coefficient

The coefficient for equilibrium partitioning of TNT from aqueous solution into the gel was determined by measuring the relative magnitude of TNT absorption in aqueous solution and in the gel for a block of gel at equilibrium with an aqueous TNT solution. For a gel prepared from 1.0 g of PVal in 18 mL of water and 160 mL of 10% glutaraldehyde, the partition coefficient was estimated to be 1.43.

#### Prospects for increasing the partition coefficient

Because the partition coefficient of the PVal gel is too low, TNT cannot be pre-concentrated to the extent required for in-situ sensing in ground water at the sub-ppm level. Several approaches to increasing the partition coefficient were consid-

ered. The ratio of PVal to water in the gel can be increased by starting with a higher initial PVal concentration or by increasing the level of glutaraldehyde to get a higher degree of cross-linking. However, higher levels of glutaraldehyde lead to higher background absorption, while formation of clear gels is more difficult at higher PVal levels because of the increased viscosity of the aqueous PVal solution and the tendency for the gel to form more rapidly.

Rather than attempt the difficult task of forming gels with higher PVal levels, a simpler experiment was performed to estimate the PVal level required to significantly increase the partition coefficient. The solubility of TNT was measured as a function of the volume percentage of ethanol added to water. Because ethanol and PVal are both aliphatic alcohols, we reasoned that the increase in solubility as a function of added ethanol should be analogous to the increase in preconcentration factors with an increased percentage of PVal in the gel.

Solubility was measured by adding solid TNT to a series of ethanol-water mixtures and shaking for 48 hr. After centrifuging to remove excess solid TNT, the TNT concentration was determined by UV absorption.

Solubility data are listed in Table 1. Although TNT is much more soluble in pure ethanol than in pure water, small amounts of added ethanol do not significantly increase the aqueous solubility of TNT. The concentration of added ethanol must be greater than 50% by volume to significantly enhance TNT solubility. Since formation of gels containing PVal concentrations approaching 50% does not appear to be feasible, we conclude that it will not be possible to prepare gels that will adequately preconcentrate TNT for the proposed sensing application.

The possibility of increasing the hydrophobicity of the gel to produce increased partitioning was also considered. This was done by reacting the gel with monofunctional aldehydes including formaldehyde, acetaldehyde and butyraldehyde. The resulting gels tended to shrink after formation and become very cloudy. They were not at all suitable for UV absorption measurements.

While the PVal gels do not have the necessary characteristics for in-situ measurements of TNT, they are useful media for optical measurements. We believe that they may prove useful for other optical sensing applications.

#### **TNT solubility in dextran**

To resolve uncertainties in the results reported in the first year of this project, the solubility of TNT was measured in concentrated dextran solutions by the same procedure used to measure TNT solubility in methanol-water mixtures. It was found that TNT is 2.1 times more soluble in a solution prepared by dissolving 4.0 g of dextran in 10 mL of water than in pure water. This indicates that concentrated dextran solutions will not adequately preconcentrate TNT. The apparent high partition coefficients measured in the first year of the project were an artifact of membrane leakage and associated problems.

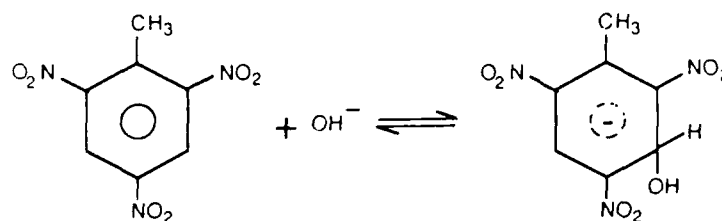
**Table 1. Relative solubility of TNT in ethanol-water solutions.**

<i>Ethanol concentration (volume %)</i>	<i>Relative solubility (normalized to 100)</i>
0	0.53
10	0.54
20	0.61
30	0.78
40	1.44
50	4.16
60	8.56
70	14.30
80	25.50
90	55.90
100	100.00

## SENSING BASED ON TNT ANION FORMATION

### Background

Because of the strong electron withdrawal character of nitro groups, TNT is a fairly strong acid, reacting with hydroxide in an aqueous base to form a colored anion as shown below:



The negative charge on the anion is resonance stabilized through all three nitro groups. The anion has a strong absorption band in the visible spectrum from 460 to 520 nm. Solutions of the anion are brownish red in color. Formation of the TNT anion has been exploited to develop a method for field measurement of TNT concentrations (Heller et al. 1982).

Measurements in the visible region of the spectrum offer important advantages relative to measurements in the ultraviolet below 300 nm. Less expensive optical components can be used, including incandescent sources and glass optical fiber. Optical fiber transmission is much higher in the visible than in the ultraviolet. Furthermore, background absorption is less likely to be a problem in the visible region of the spectrum. Because of these advantages, a series of experiments were performed to assess the feasibility of optically sensing TNT via the anion.

### Anion formation experiments

Addition of sufficient sodium hydroxide to bring the pH of an aqueous 4-ppm TNT solution above 10.5 causes observable color but the color tends to fade upon standing. The absorbance increases with increasing amounts of added sodium hydroxide up to a concentration of 0.012 M. This is illustrated by Table 2, which lists the absorbances of a 4-mg/L aqueous TNT solution at 465 nm for varying amounts of added base. This we attribute to more complete conversion of TNT to the anion. The pKa for TNT is estimated to be approximately 11.

**Table 2. Absorbance of 4 mg/L of aqueous TNT solution after NaOH addition.**

Final NaOH Conc (millimolar)	Absorbance after 10 min	Absorbance after 20 min
1.2	0.082	0.082
2.4	0.120	0.120
4.0	0.138	0.136
8.0	0.158	0.153
12.0	0.158	0.148
20.0	0.162	0.148
40.0	0.122	0.098
1.2 + PEI*	0.192	0.188

Absorbances were measured at 465 nm using 1.00-cm cuvetts and a Spectronic 200 spectrophotometer.

\* The final concentration of this sample contained 0.5% poly-ethylenimine in addition to 1.2-mM NaOH.

Absorbance of each solution was measured both 10 and 20 minutes after adding a base to get an estimate of the rate of fading. The rate increased at very high pH, as evidenced by increasing differences between absorbances measured 10 and 20 min after the addition of base. At the highest levels of added base, significant fading occurred before the initial absorbance measurement.

Table 2 also includes data for a solution to which both sodium hydroxide and polyethylenimine were added. Polyethylenimine is a polymeric aliphatic amine that will be partially protonated even at pHs above 10. In the presence of polyethylenimine the absorbance was enhanced, indicating a higher percentage of TNT converted to the anion. We believe two mechanisms are operating here: an electrostatic attraction between the negative charge on TNT and the positive charge on polyethylenimine, and a hydrophobic attraction between the rest of the TNT molecule and the polyethylenimine backbone. These combined interactions enhance the tendency of TNT to dissociate to the anion.

Because cationic organic polymers enhance formation of hydrophobic counterions, some experiments were performed to determine the pH necessary to convert TNT to the anion in the presence of anion exchangers. Both Amberlite 21637 and Rexyn 201 bound TNT, forming a reddish anion that could be observed visually at pHs as low as 8. Thus anion exchange resins could serve to sense TNT in media of constant high pH. However, they are not suited for generalized TNT detection in ground water because pH values below 8 are commonly encountered. Consequently, this approach was abandoned in favor of an alternate approach that would not be as pH dependent.

## **SENSING WITH AMINE LOADED PVC MEMBRANES**

### **Background**

Because the above-mentioned approaches to TNT sensing have serious limitations, an alternative was sought. It is known that nitroaromatics form charge transfer complexes with amines in chloroform (Vasundra and Parihar 1980). These complexes have long wavelength absorption bands associated with charge transfer from the amine to the electron withdrawing nitroaromatic. Our goal was to base sensing on the formation of the charge transfer band. Polyvinyl chloride (PVC) was chosen as the indicator matrix because it is chemically similar to chloroform. Dioctyl phthalate, a common plasticizer, was added to produce a flexible membrane that would allow for nitroaromatic diffusion within the membrane.

Experimentally it was found that when primary amines were added to plasticized PVC, the resulting membrane reacted with TNT to form a brown color. Because color formation does not appear to be reversible, we now believe this color is due to an addition product rather than a charge transfer complex. It has been previously demonstrated that certain nitroaromatics react with amines to form colored products in nonaqueous media (Glover and Kayser 1968). Although the reaction does not seem to be reversible, the amine-loaded PVC membranes offer several attractive features for sensing. The change in absorbance occurs at long wavelengths which allow for convenient sensing through optical fiber. The response to TNT has adequate potential sensitivity for ground water sensing applications and it is not dependent on pH in the range expected for most ground water. Consequently, we investigated this approach to sensing in some depth.

### **Membrane preparation**

A typical membrane preparation is as follows: 1.0 gram of an emulsion polymerized PVC powder is dissolved in 40 mL of tetrahydrofuran (THF). Then 0.8 mL of dioctyl phthalate (DOP) and 0.5 mL of an amine are added. Unless other-

wise specified the amine was N,N-diethylethylenediamine. After mixing, the solution is placed in a 9-cm-diam glass petri dish and covered with Kimwipes that are held in place. This reduces the rate of solvent evaporation and minimizes absorption of ambient water. About 30 hr is required for solvent evaporation. Measurements were made with 4-mm-diam disks of membrane removed from the bottom of the petri dish with a cork borer.

It is critical that the membrane be dry during preparation, because water causes the PVC to be cloudy. To exclude moisture, we covered the container used to dissolve PVC in THF with an airtight laboratory film during the dissolution step. Gentle heating is applied to facilitate complete PVC dissolution before adding DOP and the amine.

#### Effect of amine structure

Membranes were prepared using a variety of amines. Table 3 qualitatively summarizes the results. Strongest color response was observed for lipophilic primary amines. Weaker response was observed for a lipophilic secondary amine, dibutyl amine. Tertiary amines did not produce any detectable color. The response was weak for ethylenediamine and diethylamine. Because these are small, highly water soluble amines, we believe that they are rapidly extracted into water where the reaction with TNT does not occur. Two amines, 4,9-dioxa-1,12-dodecanediamine and tri(2-aminoethyl)amine, failed to yield clear membranes. Apparently, these amines aggregate while THF is evaporating, producing microdomains in the membrane.

Table 3. Effect of amine structure on membrane response.

<i>Amine</i>	<i>Structure</i>	<i>Response</i>
N, N-diethylethylenediamine	$(C_2H_5)_2N(CH_2)_2NH_2$	Strong color
2-methyl-1, 5-diaminopentane	$H_2NCH_2CH(CH_3)(CH_2)_3NH_2$	Baseline
dibutylamine	$(C_4H_9)_2NH$	Medium color
ethylenediamine	$H_2N(CH_2)_2NH_2$	Weak color
diethylamine	$(C_2H_5)_2NH$	Weak color
trioctylamine	$(C_8H_{17})_3N$	No color
triethylamine	$(C_2H_5)_3N$	No color
tri(2-aminethyl)amine	$(H_2NCH_2CH_2)_3N$	Cloudy membrane
3-diethylaminopropylamine	$(C_2H_5)_2N(CH_2)_3NH_2$	Strong color
3-diethylaminopropylamine	$(C_4H_9)_2N(CH_2)_3NH_2$	Strongest color
4,9-dioxa-1,12-dodecanamine	$H_2N(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$	Cloudy membrane

The best response of all the amines tried to date was observed for 3-dibutyl-amino-propylamine. However, this was discovered only very recently after most experiments were performed using N,N-diethylethylenediamine.

## Membrane characterization

### *Spectral properties of the membrane*

Membranes added to aqueous TNT solutions become visibly brown when the TNT concentration exceeds 2 ppm. The color becomes gradually deeper with increasing exposure time. Two approaches were used to determine the spectral distribution of the color so that the optimum wavelength for TNT sensing could be established. One approach was to use a bifurcated fiber optic photometer as shown in Figure 4. Separate fibers conduct light to and from the membrane, which is placed on the common end of the bifurcated bundle. Plasticized membranes adhere to the bundle without any adhesive or other means of holding the membrane in place. As shown in the figure, part of the light will be reflected at the membrane surface because the refractive index changes at this point. Some of this light is redirected toward the return fibers. Measurements were made with the membrane in air. In water the change in refractive index at the membrane surface will be less and a lower percentage of light will be reflected. This will affect absolute intensities but should not affect the absorbance of the membrane. A series of interference filters were placed in the optical path to vary wavelength.

The second approach was to place the membrane in the sample compartment of a Perkin-Elmer spectrofluorometer. The excitation and emission monochromators were set to the same wavelengths so that the reflected intensity was measured. Wavelength was varied to get a spectrum.

For both approaches, reflected intensities were measured for a membrane exposed for one hour to an aqueous 8-mg/L TNT solution buffered to pH 7. These intensities were designated "*I*." Reference intensities,  $I_0$ , were determined for

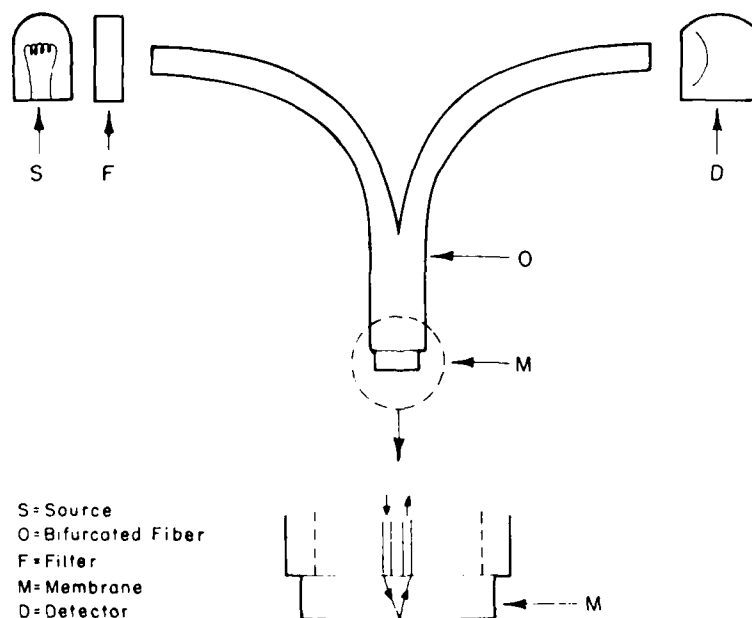
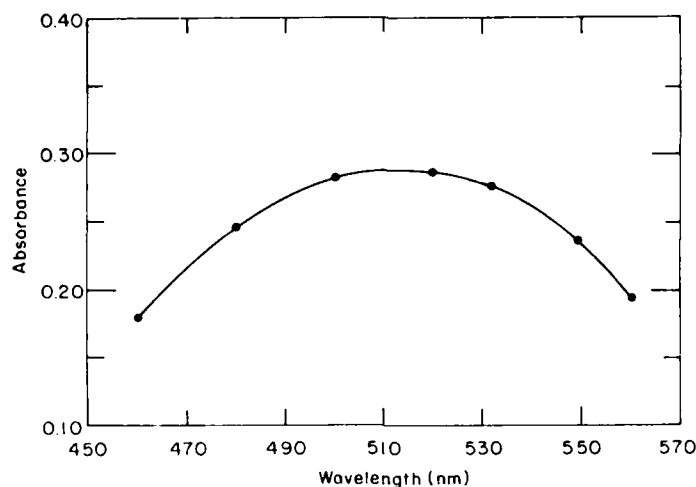
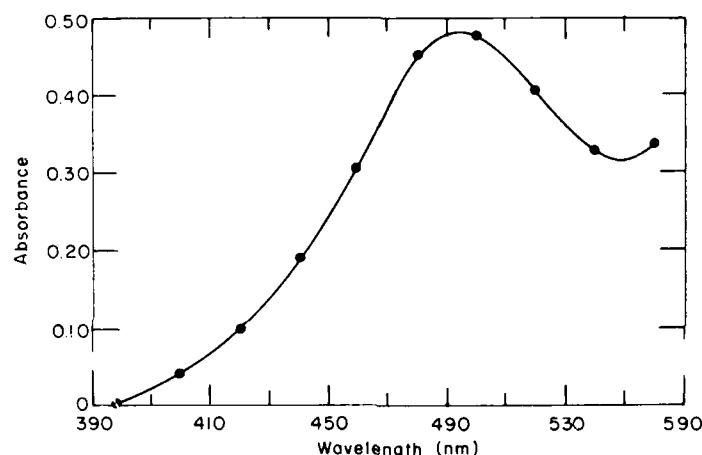


Figure 4. Diagram of fiber optic photometer including close-up of sensor end, illustrating optical path.





*a. Absorption spectrum of membrane exposed to 8 mg/L of TNT measured using fiber optic photometer.*



*b. Reflectance spectrum of membrane exposed to 8 mg/L of TNT measured by conventional spectrofluorometer.*

**Figure 5. Absorption and reflectance spectra of the membrane.**

membranes exposed for 1 hr to the buffer only. Figures 5a and 5b show spectra for both approaches plotted as  $\log I_0/I$  vs wavelength in nm. While the two spectra differ somewhat, both show maximum response around 520 nm, the wavelength used for subsequent measurements. As noted below, response to TNT obeyed Beer's law when measured with the fiber optic photometer. Thus, we believe that this measurement accurately represents the absorbance of the membrane.

The spectrum taken with the fiber optic photometer was limited to the wavelength range from 460 to 560 nm because of filter availability. The spectrum taken with the spectrofluorometer, however, extends to 400 nm where there is no observable absorbance. Thus, an absorbance measurement at 400 nm can serve as a reference to determine the spectral properties of the membrane independent of TNT concentration. The measured parameter would be the ratio of intensities at 400 and 520 nm.

The spectrum of the membrane exposed to TNT differs from absorption spectra of both charge transfer complexes and the TNT anion. It is somewhat similar to spectra for nitroaromatic-amine addition products (Glover and Kayser 1968).

#### *Effect of DOP concentration*

A series of membranes were prepared using 0.5 g PVC, 0.25 mL of amine and 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mL of DOP. The membrane without DOP was stiff and did not respond to TNT. Data for the other membranes are summarized in Table 4. Reflected intensities were measured using the fiber optic photometer shown in Figure 4 for duplicate membranes exposed for 40 min to either 8 mg/L of TNT or an aqueous blank.

The ratio of blank to TNT intensities is a measure of the response to TNT. Response was similar for membranes prepared using 0.2 and 0.4 mL of DOP. Although the response was slightly less for 0.4 mL of DOP, these membranes were more flexible and easier to handle than the membranes with only 0.2 mL of DOP. Therefore, a ratio of 0.4 mL DOP/0.5 g PVC (or 0.8 mL DOP/g PVC) was used in subsequent membrane formulations.

Membranes with higher levels of DOP also respond to TNT. However, these membranes tend to become increasingly cloudy with time. This causes an increase in the radiation scattered back to the detector which is observed as an increase in blank intensity. Therefore, these membranes are not well suited for sensing.

The data also illustrate precision of the intensity measurements. Agreement between replicates was surprisingly good, considering that each measurement was made with a separate membrane independently attached to the common end of the bifurcated fiber optic bundle.

#### *Effect of amine concentration*

Membranes were prepared with 0.5 g of PVC, 0.4 mL of DOP and 0.2, 0.4, 0.6, 0.8 and 1.0 mL of N,N-diethylethylenediamine. No significant difference in response was observed from membrane to membrane. Since 0.2 mL of amine is sufficient for maximum response, it was used in subsequent membrane formulations.

#### *Effect of membrane thickness*

Membrane thickness was varied by keeping the ratio of membrane components constant but changing the total amounts.

Table 5 shows intensities for membranes prepared using 0.25, 0.5, 1.0, 1.5 and 2.0 g of PVC. Intensities are for membranes exposed either to 8 mg/L of aqueous TNT or to an aqueous blank for 40 min. The thicknesses were calculated from the known volumes of DOP and amine and the known amount of PVC.

**Table 4. Effect of DOP level on intensities reflected from membranes for two replicate measurements.**

<i>DOP Level (mL)</i>	<i>Blank (I<sub>0</sub>)</i>	<i>TNT (I)</i>	<i>Log I<sub>0</sub>/I</i>
0.2	5.0, 4.9	2.1, 1.8	0.40
0.4	5.4, 4.8	2.3, 1.8	0.37
0.6	9.8, 9.5	5.4, 5.1	0.26
0.8	10.8, 10.9	6.7, 6.5	0.21
1.0	14.2, 14.4	8.8, 13.2	0.11

Light intensities are in relative units.

**Table 5. Effect of membrane thickness on reflected intensities.**

<i>Thickness (mm)</i>	<i>Blank (I<sub>0</sub>)</i>	<i>TNT (I)</i>	<i>Log I<sub>0</sub>/I</i>
0.09	2.8, 3.3	2.5, 3.0	0.41
0.18	7.1, 6.7	3.9, 4.1	0.23
0.36	9.4, 8.8	4.3, 3.3	0.32
0.54	17.0, 17.0	12.0, 9.3	0.20
0.72	18.5, 18.8	10.4, 7.8	0.30

Light intensities are in relative units.

Absolute intensities increased with membrane thickness, due to an optical effect. Source light diverges as it leaves an excitation fiber and the extent of beam divergence increases with membrane thickness. With thin membranes, beam divergence is slight and most of the light gets reflected back into the excitation fiber, rather than entering a fiber that leads to the detector. However, with thick membranes significant divergence occurs, causing an increase in the percentage of light that gets reflected into fibers that lead to the detector.

Although absolute intensities increase with membrane thickness, the TNT absorbance does not show a strong systematic dependence on thickness. The amount of colored product is independent of thickness because the color-forming reaction occurs at the surface where the membrane contacts the TNT solution. Therefore, the color depth will depend on how far TNT diffuses into the membrane. The fact that the absorbance does not vary with membrane thickness indicates that the color depth is less than the membrane thickness, even for the thinnest membrane.

All other experiments were performed using a 0.36-mm-thick membrane because it is convenient to prepare and handle.

#### *Effect of pH*

Membranes were exposed to acetate buffered solutions adjusted to pHs 4.0 and 5.0 and phosphate buffered solutions adjusted to pHs 6.0, 7.0 and 8.0. Table 6 shows measured intensities using the fiber optic photometer for membranes exposed for 40 min to either an aqueous 8-ppm TNT solution or an aqueous blank. As pH decreased, absolute intensities increased but absorbances decreased, particularly at pH 4 and 5. At these pHs the membranes tend to become cloudy fairly rapidly, causing the increase in blank signal. Also the membranes become stiff and difficult to handle. The cause of the problems at low pH is unknown but we believe it may be related to the increased tendency of amines to protonate at low pH, which enhances the rate at which water enters the membrane. We hope that this problem can be eliminated by appropriate choice of membrane formulation. The color-forming reaction itself does not seem to be directly affected by pH, as evidenced by the observation that the absolute difference between blank and sample intensities does not change significantly with pH.

**Table 6. Effect of pH on reflected intensities for the replicate measurements.**

<i>pH</i>	<i>Blank</i> ( $I_0$ )	<i>TNT</i> ( $I$ )	<i>Log I<sub>0</sub>/I</i>
4.0	12.1, 11.6	7.0	0.23
5.0	11.8	7.3, 7.4	0.20
6.0	9.0, 9.1	4.0, 4.9	0.30
7.0	9.0, 9.3	3.7, 3.8	0.38
8.0	8.8, 9.7	4.0, 3.5	0.40

Light intensities are in relative units.

#### *Response to TNT*

Figure 6 shows a plot of the log of the blank intensity/intensity in the presence of TNT ( $I_0/I$ ) measured as a function of TNT concentration with the fiber optic photometer. The plot is linear through the origin, indicating adherence to Beer's law. This suggests that the measured parameter is absorbance. As suggested in Figure 4, we believe that the incident light reflects off the membrane interface returning to the fiber bundle. In effect, the light passes through the membrane twice on its way to the detection system.

It should be noted that the data for Figure 6 are not a unique occurrence. Similar plots were obtained in other experiments. This confirms the reproducibility of absorbance measurements even when using separate pieces of membrane for each measurement.

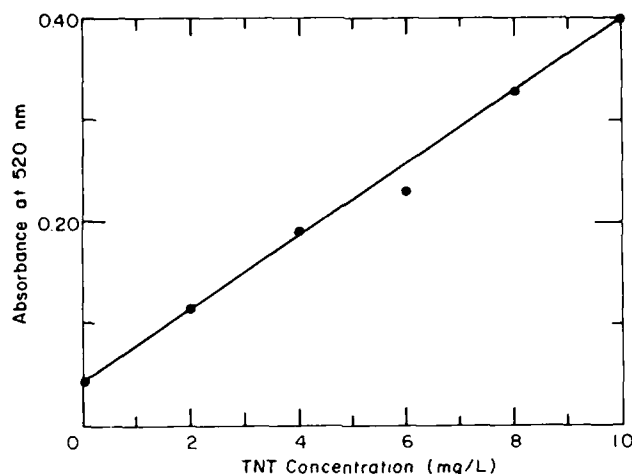


Figure 6. Absorbance at 420 nm vs TNT concentration (mg/L) for 40-min membrane exposure measured with fiber optic photometer.

The detection limit for TNT is on the order of 0.5 mg/L TNT in water, assuming a minimum detectable absorbance of 0.02. This detection limit was obtained after exposing the membrane to a TNT solution for 40 min. Membranes exposed to TNT for several days become gradually darker, indicating that the color-forming reaction continues although at a reduced rate. This in turn indicates that detection limits can be reduced to lower levels, if membranes are exposed to samples for longer time intervals.

#### Reversibility

The reversibility of response was tested by taking a membrane that had been preexposed to TNT and placing it in an aqueous buffer with no TNT. No decrease in the intensity of membrane color could be observed, indicating that the color-forming reaction is not reversible.

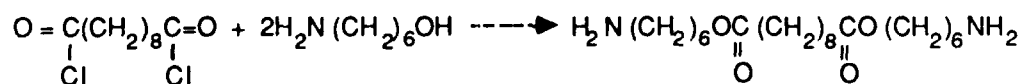
#### Response to RDX

The membranes do not respond to RDX. The earlier report of the reaction between nitroaromatics and amines also noted that RDX did not react (Glover and Kayser 1968). This supports our belief that response is due to an irreversible addition reaction to the electron-deficient aromatic ring.

#### Stability

The membranes are stable for days (and possibly longer) in sealed containers. However, in air and water they are unstable with respect to loss of amine. When open to the air, the amine vaporizes at a rate that depends on the volatility of the amine. In water, amine is extracted out of the membrane. Thus, membranes preexposed to water lose amine and lose their ability to respond to TNT. This is the major problem to be addressed in further development of TNT-sensitive amines.

In order to improve the stability of membranes, the primary amine group needs to be incorporated either into the polymer or the plasticizer. Efforts to date have been directed toward preparation of an amine-containing plasticizer. Since esters of sebacic acid are plasticizers, we have reacted 1-hydroxyoctanamine with sebacoyl chloride to prepare the amino ester. The overall reaction is shown below:



Because the amine group reacts more rapidly than the hydroxyl group with sebacoyl chloride, this reaction has to be done in three steps. The first step is to protect the amine group. The 1-hydroxyoctanamine is then reacted with sebacoyl chloride to form the ester. The final step is to remove the protecting group from the amine, leaving the desired product.

We have completed the above synthesis; the product is a solid with a melting point of 78–79°C that is soluble in chloroform but not in THF. PVC, on the other hand, is soluble in THF but not in chloroform. Both PVC and the amino ester of sebacic acid have limited solubility in chloroform/THF mixtures. Thus, to date, we have not succeeded in finding a membrane formulation that yields a satisfactory PVC membrane.

## DISCUSSION AND CONCLUSION

We have succeeded in developing a clear membrane that reacts with TNT to form a colored product. Because the reaction is irreversible, the membrane can be used only for sensing on an integrating basis.

Although the mechanism of membrane response is unknown, we have sufficient data to propose a model. The observation that response (absorbance) to TNT is independent of membrane thickness indicates that the initial color-forming reaction is occurring at the membrane surface rather than being uniformly distributed through the membrane. This is expected since typical diffusion coefficients in PVC are on the order of  $10^{-7}$  cm<sup>2</sup>/s. Given the thickness of the membrane, the exposure time in most experiments, 40 min, is insufficient for significant TNT penetration into the interior of the membrane.

Visually, response is relatively rapid at first. It then slows, reaching a reproducible value at 40 min. However, slow response continues, as evidenced by further darkening of membranes exposed to TNT for 24 hr or more. We hypothesize that the initial response involves the reaction of TNT with amine at or near the membrane surface. Further reaction is slower because TNT has to diffuse farther into the membrane.

Because the degree of color formation is independent of the amount of amine in the membrane, we believe that the rate of response is governed by TNT mass transfer into the membrane rather than the kinetics of the color-forming reaction. Mass transfer in the aqueous phase itself is not believed to be a significant component of the response rate. This is an important observation for the proposed application, since it means that membrane response will not be influenced by convection in ground water samples.

## FUTURE WORK

Before attempting further characterization of our present membranes, we believe that the primary effort should be directed toward improving membrane stability. The best way to do this is to incorporate the amine group into either the plasticizer or the polymer. Once the membrane has been stabilized, we can conduct further experiments to confirm the mechanism of membrane response and to characterize long-term response to TNT. In particular, we want to demonstrate that the membranes will respond to lower levels of TNT if allowed a sufficiently long exposure time.

## LITERATURE CITED

- Glover, R.J. and E.G. Keyser** (1968) Quantitative spectrophotometric analysis of polynitroaromatic compounds by reaction with ethylene diamine. *Analytical Chemistry*, **40**: 2055-2058.
- Heller, C.A., S.R. Grenl and E.D. Erickson** (1982) Field detection of 2,4,6-trinitrotoluene in water by ion-exchange resins. *Analytical Chemistry*, **54**: 286-289.
- Higuchi, A. and T. Iijima** (1985) Investigation of the states of water in poly(vinyl-alcohol) membranes. *Polymer*, **26**: 1207-1211.
- Shane, E.C., M.S. Girardi, C.L. Grant and W.R. Seitz** (1985) Development of a fiber optic sensor for in-situ measurements of TNT and RDX in groundwater. Final Report for Contract DACA89-85-K-0005.
- Vasundhara, T.S. and D.B. Parihar** (1980) Studies of pyrazines as their n-pi charge-transfer complexes with some nitroaromatic compounds. *Journal of Chromatography*, **194**: 254-261.
- Walsh, J.T., R.C. Chalk and C.M. Merritt** (1973) Application of liquid chromatography to pollution abatement studies of munition wastes. *Analytical Chemistry*, **45**: 1215-1220.

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